

26 AUG 2002

SPECIFICATION



166166

CURABLE MOLDING MATERIAL



G00002

AND

PROCESS FOR PRODUCING MOLDED PRODUCT

TECHNICAL FIELD

This invention relates to a molding material for producing a molded product from metathesis-polymerizable cycloolefins, and a process for producing a molded product from the molding material.

BACKGROUND ART

Cycloolefins are known to undergo ring-opening polymerization in the presence of a metathesis (double decomposition) catalyst system. For example, J. Am. Chem. Soc., Vol. 82, page 2337 (1960) discloses that norbornene undergoes ring-opening polymerization in the presence of a metathesis catalyst system. Angew. Chem. Int. Edn., Vol. 3, page 723 (1964) discloses that cyclopentene undergoes ring-opening polymerization in the presence of a metathesis catalyst system $[\text{MoCl}_5/\text{Al}(\text{C}_2\text{H}_5)_3]$.

Processes for producing polymers by subjecting cycloolefins to ring-opening polymerization are also

known in the art. For example, Japanese Patent Applications Laid-open (KOKAI) Nos. Sho50-130900 and Sho52-33000 disclose a process in which a metathesis catalyst system comprised of a halide of tungsten or molybdenum and an organoaluminum compound is used to produce a ring-opening polymerization polymer.

Meanwhile, also known are processes for producing cross-linked polymer molded products by subjecting norbornene type cycloolefins (monomers) such as dicyclopentadiene and tricyclopentadiene to bulk polymerization. For example, Japanese Patent Applications Laid-open (KOKAI) Nos. Sho58-127728 and Sho58-129013 disclose a process in which a solution A comprised of a mixture of a catalytic component of a metathesis catalyst system with a monomer and a solution B comprised of a mixture of an activator of a metathesis catalyst system with a monomer are subjected to reactive injection molding (RIM) to produce a cross-linked polymer molded product.

Japanese Patent Applications Laid-open (KOKAI) No. Sho59-51911 discloses a process in which a norbornene type monomer is subjected to reactive injection molding in the presence of a metathesis catalyst system formed by combination of a catalytic component selected from an organoammonium salt of tungsten and that of molybdenum

with an activator selected from an alkoxoalkylaluminum halide and an aryloxyaluminum halide, to produce a cross-linked polymer molded product.

Japanese Patent Applications Laid-open (KOKAI) No. Hei3-205409 discloses a process in which a metathesis catalyst system formed by combination of a catalytic component selected from tungsten hexachloride and tungsten oxytetrachloride with an activator selected from diethylaluminum chloride and ethylaluminum dichloride is used to produce a cross-linked dicyclopentadiene polymer by reactive injection molding.

In the above metathesis catalyst system, the catalytic component has become known to be activated by the activator to cause the norbornene type monomer to undergo ring-opening polymerization. Also, when the reactive injection molding is carried out, the solutions A and B are impact-mixed and the resultant mixture is immediately poured into a mold as it stands liquid to effect ring-opening polymerization in bulk.

However, the organoaluminum compound used as the activator is so highly reactive as to immediately react with water or oxygen when it is present, to lose its action of catalytic activation. Accordingly, when the reactive injection molding is carried out, the bulk polymerization must be effected in a space formed in the state a separation

type mold is closed, in order to prevent inclusion of the water and oxygen in air as far as possible. Hence, there has been a problem that molding methods and shapes of molded product are limited.

Japanese Patent Applications Laid-open (KOKAI) Nos. Hei2-225518 and Hei3-292124 disclose a process in which a norbornene type monomer is subjected to bulk polymerization in a mold to prepare a primary molded product and then the primary molded product is secondarily molded (shaped).

However, in the process in which such a primary molded product is prepared, the primary molded product has completely undergone metathesis reaction to become hard, and can not be deformed with ease. Accordingly, the primary molded product must be shaped after it has been heated to a high temperature (usually 100°C or above), bringing about various problems such that labor is required at the time of the secondary molding. Also, since the primary molded product is a cured product having completely undergone metathesis reaction, it has been difficult to mold it into complicated shapes in the secondary molding.

DISCLOSURE OF THE INVENTION

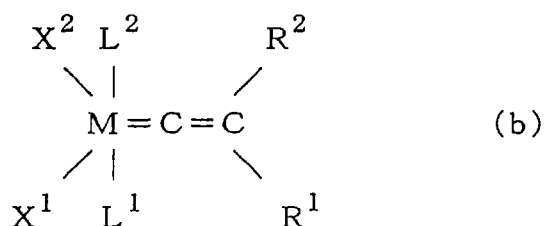
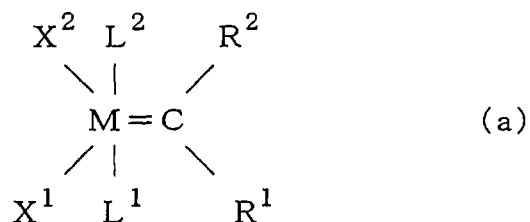
The molding material of the present invention is a

curable molding material made semi-cured by allowing a metathesis-polymerizable cycloolefin to react in the presence of a metathesis polymerization catalyst.

The molded product may preferably have the shape of at least one selected from a plate, a sheet and a rod.

As the metathesis-polymerizable cycloolefin, at least one selected from a bicyclic or more-cyclic norbornene and a monocyclic cycloolefin having 4 or more carbon atoms may preferably be used.

As the metathesis polymerization catalyst, at least one of metathesis polymerization catalysts represented by the following Formulas (a) and (b) may preferably be used.



In Formulas (a) and (b);

M represents a ruthenium atom or an osmium atom;

R¹ and R² each independently represent a group selected from a hydrogen atom, an alkyl group having 1 to 20 carbon

atoms, an alkenyl group having 2 to 20 carbon atoms, an alkynyl group having 2 to 20 carbon atoms, an aryl group, a carboxylate group having 1 to 20 carbon atoms, an alkoxyl group having 1 to 20 carbon atoms, an alkenyloxy group having 2 to 20 carbon atoms, an aryloxy group, an alkoxycarbonyl group having 2 to 20 carbon atoms, an alkylthio group having 1 to 20 carbon atoms, an alkylsulfonyl group having 1 to 20 carbon atoms, an alkylsulfinyl group having 1 to 20 carbon atoms, an alkylseleno group having 1 to 20 carbon atoms, an alkylseleninyl group having 1 to 20 carbon atoms and an alkylselenonyl group having 1 to 20 carbon atoms, each of which may be substituted with an alkyl group having 1 to 5 carbon atoms, a halogen atom, an alkoxyl group having 1 to 5 carbon atoms or a phenyl, where the phenyl may be substituted with a halogen atom, an alkyl group having 1 to 5 carbon atoms or an alkoxyl group having 1 to 5 carbon atoms;

X^1 and X^2 each represent an anionic ligand; and

L^1 and L^2 each represent a neutral electron-donating group.

The process of the present invention for producing a molded product comprises subjecting the above curable molding material to heat curing so as to be shaped into a preset form. The production process of the present

invention has a first step of preparing a molding material, and a second step of shaping the molding material into a preset form, followed by heat curing.

The metathesis-polymerizable cycloolefin is allowed to react in the presence of a metathesis polymerization catalyst to form a molding material standing semi-cured, and the molding material may be introduced into a mold while the molding material is kept semi-cured, followed by curing to produce a molded product.

As the mold for molding, a mold for compression molding may be used so that the molding can be carried out in the atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustration (cross-sectional diagrammatic view) showing a step in the production of a molded product by means of a mold for compression molding, using a semi-cured material. In Fig. 1, reference numeral 1 denotes the semi-cured material; reference numeral 2, a bottom force (female mold) for compression molding; reference numeral 3, a top force (male mold) for compression molding; reference numeral 4, a compression molding equipment for SMC (sheet mold compound); and reference numeral 5, the atmosphere.

BEST MODES FOR PRACTICING THE INVENTION

As the metathesis-polymerizable cycloolefin used in the present invention, at least one selected from a bicyclic or more-cyclic norbornene and a monocyclic cycloolefin having 4 or more carbon atoms may be used. In particular, norbornenes such as substituted or unsubstituted norbornenes, dicyclopentadiene and dihydrodicyclopentadiene may preferably be used.

Norbornenes may include;

bicyclic norbornenes such as norbornene,
norbornadiene, methyl norbornene, dimethyl norbornene,
ethyl norbornene, ethylidene norbornene, butyl norbornene,
5-acetyl-2-norbornene,
dimethyl-5-norbornene-2,3-dicarboxylate,
N-hydroxy-5-norbornene-2,3-dicarboxyimide,
5-norbornene-2-carbonitrile,
5-norbornene-2-carboxyaldehyde,
5-norbornene-2,3-dicarboxylic acid monomethyl ester,
5-norbornene-2,3-dicarboxylic acid dimethyl ester,
5-norbornene-2,3-dicarboxylic acid diethyl ester,
5-norbornene-2,3-dicarboxylic acid di(n-butyl) ester,
5-norbornene-2,3-dicarboxylic acid dicyclohexyl ester,
5-norbornene-2,3-dicarboxylic acid dibenzyl ester,
5-norbornene-2,3-dicarboxylic acid anhydride,
3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride,

5-norbornene-2,3-dicarboxylic acid,
 5-norbornene-2-methanol, 6-triethoxysilyl-2-norbornene
 and 5-norbornene-2-ol;

tricyclic norbornenes such as dicyclopentadiene
 (i.e., cyclopentadiene dimer), dihydrodicyclopentadiene,
 methyldicyclopentadiene and dimethyldicyclopentadiene;

tetracyclic norbornenes such as tetracyclododecene,
 methyltetracyclododecene and dimethylcyclotetradodecene;
 and

penta- or more-cyclic norbornenes such as
 tricyclopentadiene (i.e., cyclopentadiene trimer) and
 tetracyclopentadiene (i.e., cyclopentadiene tetramer).

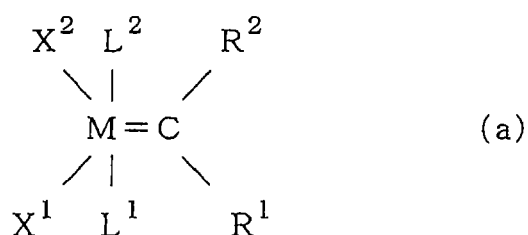
Compounds having two or more norbornene groups as
 exemplified by tetracyclododecadiene and symmetric
 tricyclopentadiene may also be used.

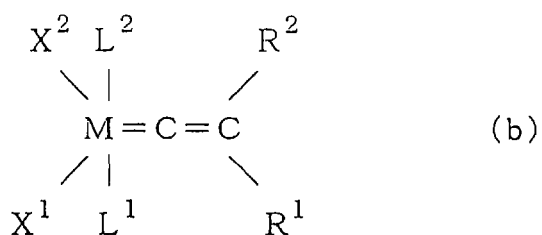
Also usable are cycloolefins other than norbornene
 types, as exemplified by cyclobutene, cyclopentene,
 cyclooctene, cyclododecene, 1,5-cyclooctadiene,
 1,3,5,7-cyclooctatetraene, 1,5,7-cyclododecatriene,
 5,6-epoxy-1-cyclooctene, 3,4-epoxy-1-cyclooctene,
 5-methoxy-1-cyclooctene, 5-bromo-1-cyclooctene,
 5-isopropoxy-1-cyclooctene, 5-formyl-1-cyclooctene,
 5-methoxy-1-cyclooctene, ethyl
 cycloocto-1-ene-5-carboxylate, trimethylsilyl
 cycloocto-1-ene-5-carboxylate, tetrahydroindene and

methyltetrahydroindene.

Any of the above compounds may be used alone or in the form of a mixture of two or more. When used in the form of a mixture of two or more, a mixture of 50% by weight or more of dicyclopentadiene and besides tricyclopentadiene and/or tetracyclopentadiene is preferred.

The metathesis polymerization catalyst used in the present invention differs from double decomposition catalysts formed of combination of a catalytic component with an activator as conventionally known. It is a catalyst capable of causing metathesis-polymerizable cycloolefin compounds to undergo ring-opening polymerization by double decomposition (metathesis) reaction without losing its catalytic activity with ease because of water and oxygen in air. What is preferable as such a metathesis polymerization catalyst is at least one of metathesis polymerization catalysts represented by the following formulas (a) and (b).





In Formulas (a) and (b);

M represents a ruthenium atom or an osmium atom;

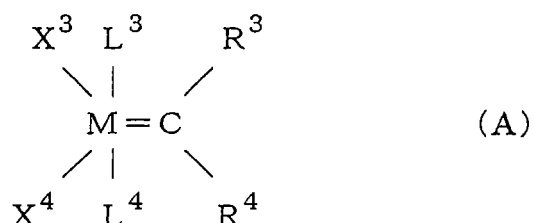
R¹ and R² each independently represent a group selected from a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, an alkynyl group having 2 to 20 carbon atoms, an aryl group, a carboxylate group having 1 to 20 carbon atoms, an alkoxyl group having 1 to 20 carbon atoms, an alkenyloxy group having 2 to 20 carbon atoms, an aryloxy group, an alkoxycarbonyl group having 2 to 20 carbon atoms, an alkylthio group having 1 to 20 carbon atoms, an alkylsulfonyl group having 1 to 20 carbon atoms, an alkylsulfinyl group having 1 to 20 carbon atoms, an alkylseleno group having 1 to 20 carbon atoms, an alkylseleninyl group having 1 to 20 carbon atoms and an alkylselenonyl group having 1 to 20 carbon atoms, each of which may be substituted with an alkyl group having 1 to 5 carbon atoms, a halogen atom, an alkoxyl group having 1 to 5 carbon atoms or a phenyl, where the phenyl may be substituted with a halogen atom, an alkyl group having 1 to 5 carbon atoms or an alkoxyl group having 1 to 5 carbon

atoms;

X^1 and X^2 each represent an anionic ligand; and

L^1 and L^2 each represent a neutral electron-donating group.

Of these metathesis polymerization catalysts, compounds (catalysts) represented by the following Formula (A) are preferred.



M represents a ruthenium atom or an osmium atom.

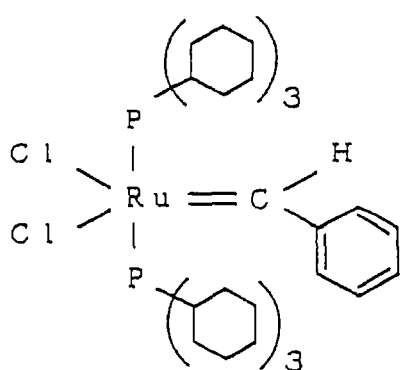
R^3 and R^4 each independently represent a hydrogen atom, an alkyl group, an alkenyl group or an aromatic group. The alkyl group may be an alkyl group having 1 to 20 carbon atoms, the alkenyl group may be an alkenyl group having 2 to 20 carbon atoms, and the aromatic group may be an aryl group. The above alkyl group, alkenyl group or aromatic group may have a substituent.

X^3 and X^4 each represent an anionic ligand, i.e., a group having negative electric charges when the coordination to the central metal is taken off, as exemplified by a hydrogen atom, a halogen, an alkyl group having 1 to 5 carbon atoms, an alkoxyl group having 1 to

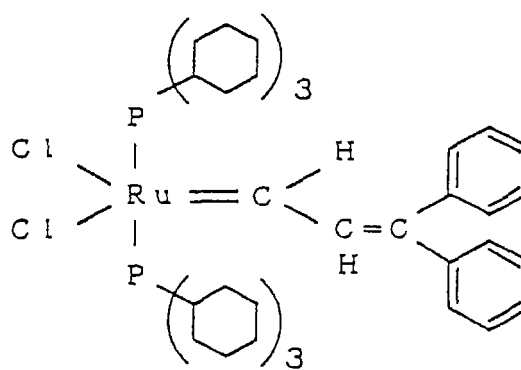
5 carbon atoms, and a phenyl group.

L^3 and L^4 each represent a neutral electron-donating group, i.e., a group having neutral electric charges when the coordination to the central metal is taken off, as exemplified by a phosphine type electron-donating group represented by $PR^5R^6R^7$ (wherein R^5 represents a secondary alkyl group or a cycloalkyl group, and R^6 and R^7 each independently represent an alkyl group having 1 to 10 carbon atoms, a cycloalkyl group, an alkoxyl group having 1 to 10 carbon atoms or an aromatic group), pyridine, and p-fluoropyridine.

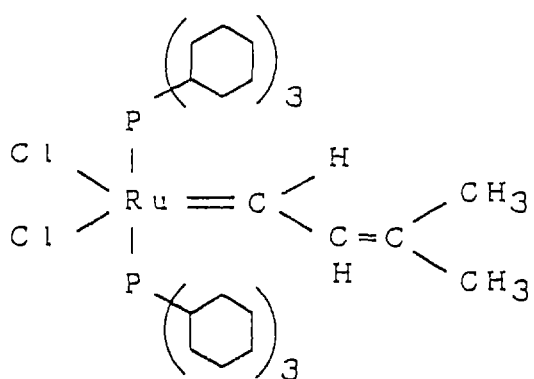
Such compounds (catalysts) may specifically include Ru carbene catalysts such as those of the following formulas (1) to (8). In particular, the compound of formula (3) is preferred.



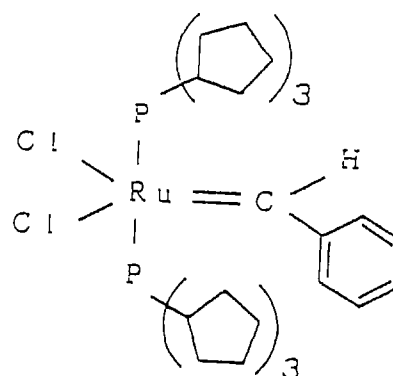
(1)



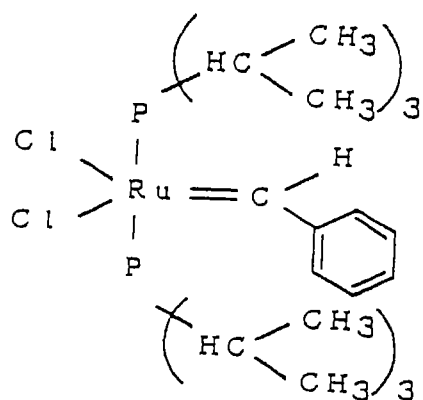
(2)



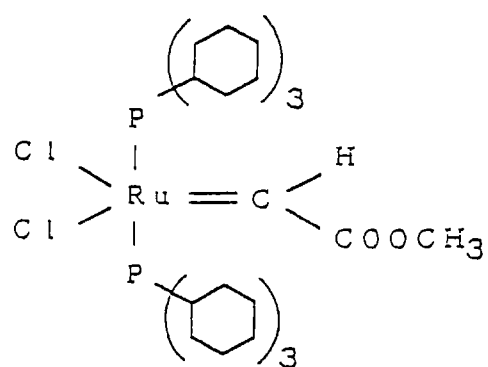
(3)



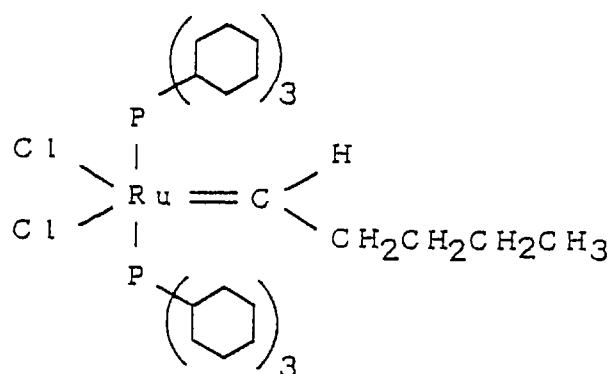
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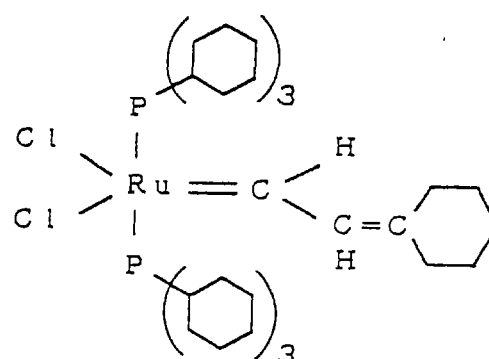
(5)



(6)



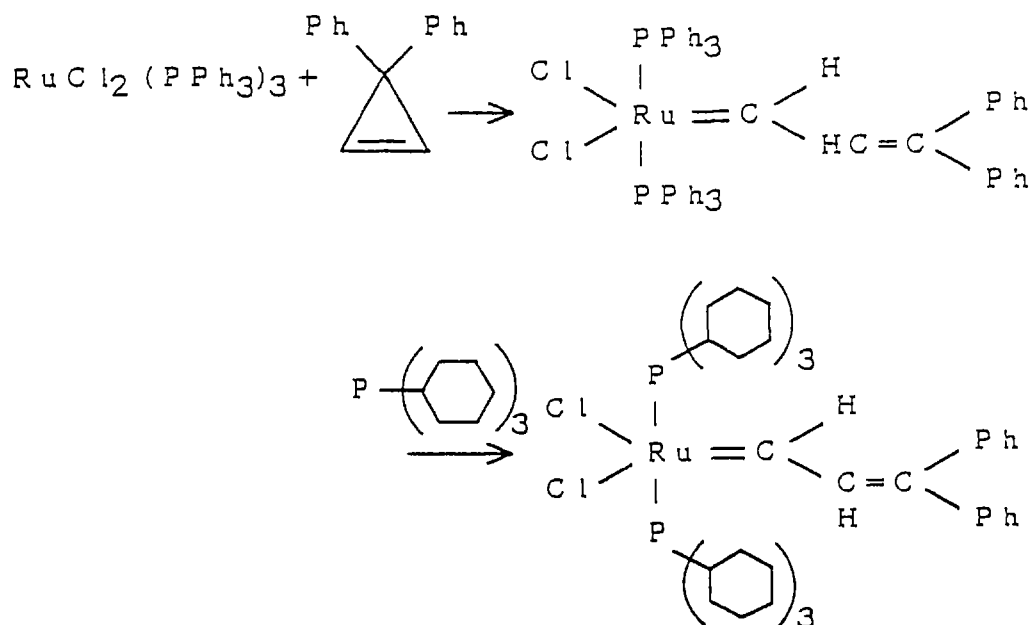
(7)



(8)

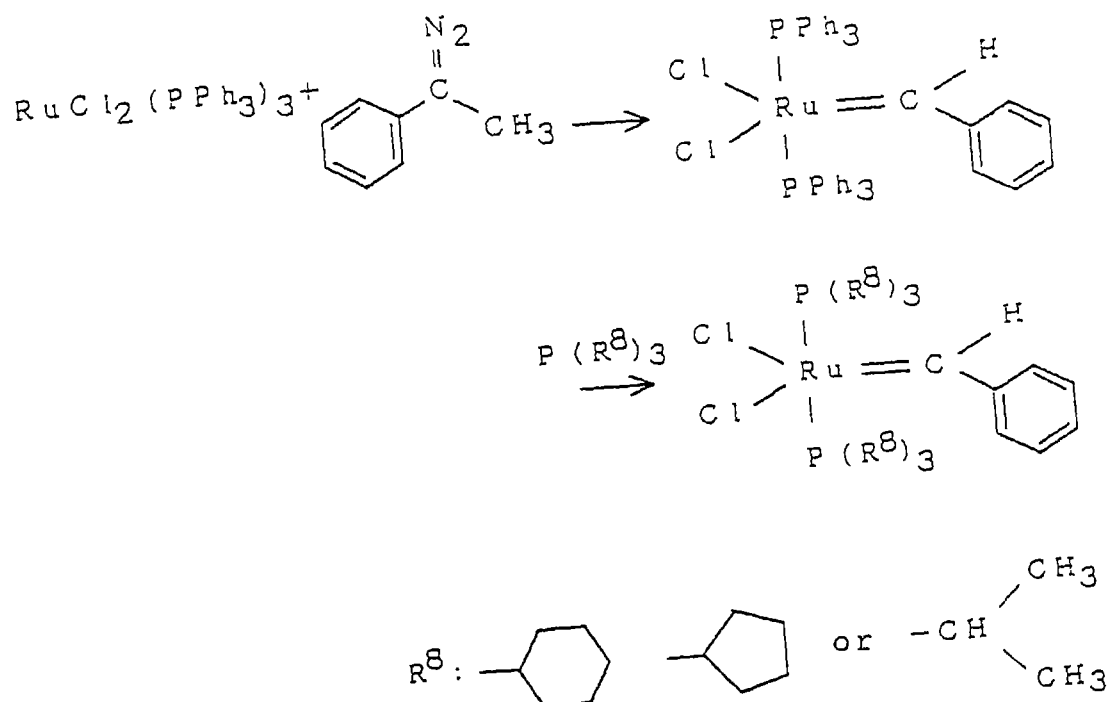
Methods for synthesizing the above compounds (catalysts) are already known in the art.

For example, Journal of American Chemical Society Vol. 118, page 100 (1996) shows a method making use of a cyclopropene derivative (Scheme 1).



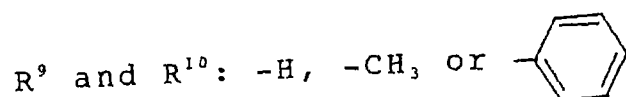
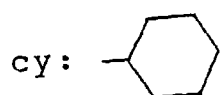
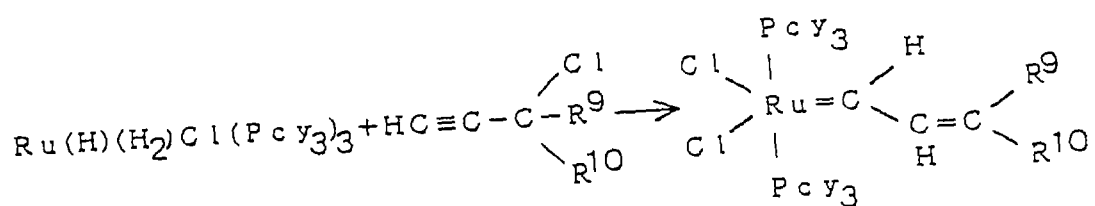
<Scheme 1>

The same publication as the above also shows a method making use of a diazo compound as shown by the following scheme (Scheme 2).



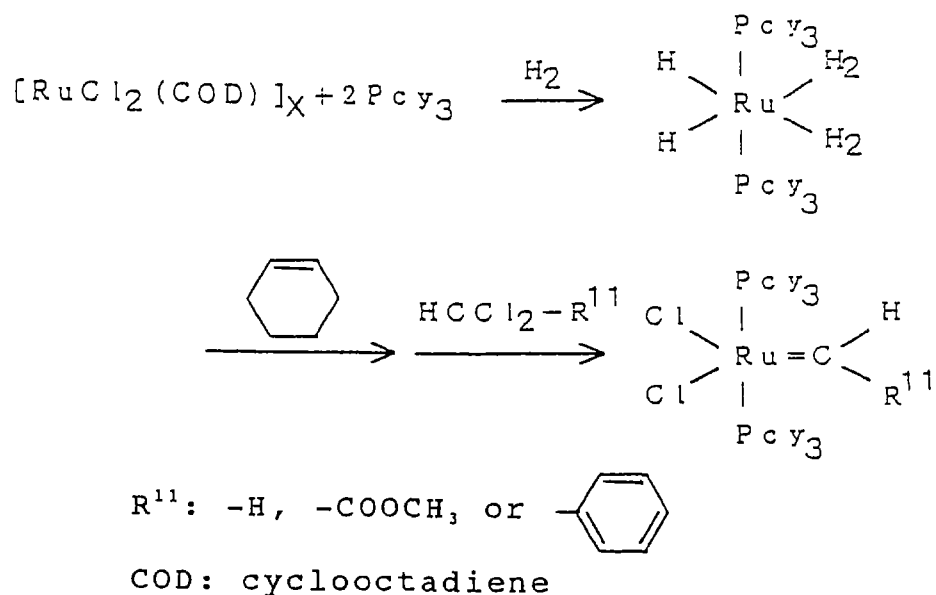
<Scheme 2>

Organometallics Vol. 16, No. 18, page 3867 (1997) also shows a method making use of propargyl chloride as shown by the following scheme (Scheme 3).

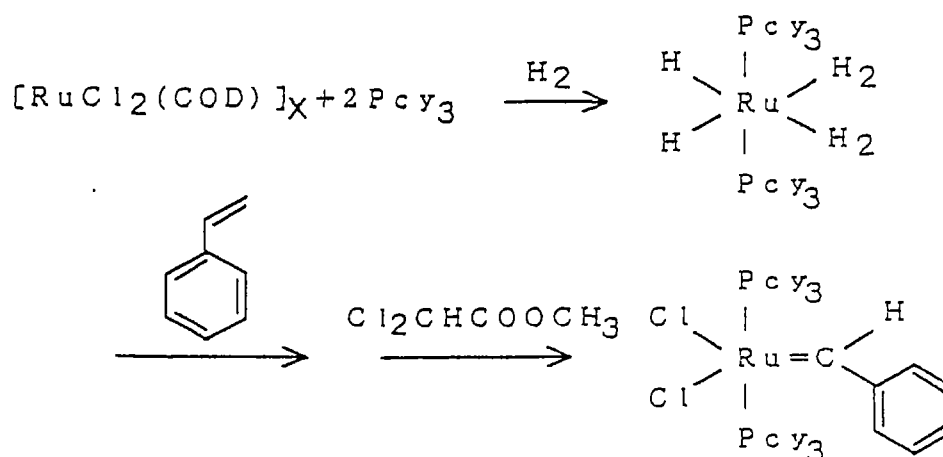


<Scheme 3>

Organometallics Vol. 16, No. 18, page 4001 (1997)
 still also shows methods as shown by the following schemes
 (Schemes 4 and 5).



<Scheme 4>



<Scheme 5>

Synthesis Example

(see Scheme 3; R^9 and R^{10} : methyl groups)

Cyclooctadiene ruthenium dichloride (21 mmol), tricyclohexylphosphine (42 mmol), sodium hydroxide (7.2 g) and 250 ml of oxygen-removed sec-butanol were put into a 500 ml Fisher-Porter bottle, and are heated at 90°C and hydrogen 2 atmospheric pressure. The pressure is repeatedly applied several times until the hydrogen is completely absorbed, and stirring is continued overnight.

In the state the pressure of hydrogen is kept applied, the reaction mixture is cooled to room temperature to obtain a yellow precipitate. With addition of 30 ml of water, the precipitate is filtered, followed by drying in a stream of hydrogen to obtain $\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{Pcy}_1)_2$ (yield: about 80%).

Next, this $\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{Pcy}_1)_2$ (1.5 mmol) is dissolved in 30 ml of dichloroethane solution, and the mixture obtained is cooled to -30°C. Then, 3-chloro-3-methyl-1-butin (1.5 mmol) is added. The solution turns purplish red immediately, which is allowed to react for 15 minutes as it is. The cooling bath is taken away, and degassed methanol (20 ml) is added, whereupon purple particles are precipitated. The particles are washed with methanol, followed by drying to obtain the desired catalyst [the compound of formula (3)] (yield: 95%). (Reference: Organometallics Vol. 16, No. 18, page 3867, 1997)

The metathesis polymerization catalyst may be used alone or in combination of two or more types. Here, the catalyst may be in an amount of from 0.001 to 20 parts by weight, and preferably from 0.01 to 5 parts by weight, based on 100 parts by weight of the metathesis-polymerizable cycloolefin.

Use of the metathesis polymerization catalyst as described above enables any desired regulation of polymerization (metathesis) reaction under appropriate selection of conditions such as amount of the catalyst used, reaction temperature and use of any reaction regulator (inhibitor). Hence, an intermediary state can be made up in which the polymerization (metathesis) reaction of the material cycloolefin has not gone to completion. Such a state is called "semi-cured". Upon the heating of a molding material standing semi-cured, the polymerization (metathesis) reaction proceeds again, and the curing can be completed.

The molding material standing semi-cured is in a liquid state, having a fluidity, or in a solid state, having no fluidity. Either state may appropriately be selected in accordance with the manner of shaping. In the case when the molding material standing semi-cured is in a liquid state, it usually has a viscosity of tens of poises or higher, which may appropriately be selected in

accordance with the manner of shaping.

In the case when the molding material standing semi-cured is in a solid state, it may have any hardness (flexural rigidity) without any particular limitations, and, which may appropriately be selected in accordance with the manner of shaping.

The viscosity or hardness of this molding material standing semi-cured may also be designed and adjusted within any desired ranges under appropriate selection of conditions such as amount of the catalyst used, reaction temperature and use of any reaction regulator (inhibitor).

Also, the time to be taken after the material is made semi-cured and until it is shaped into a preset form is appropriately selected in accordance with the form of manufacture. Incidentally, the time for which the semi-cured state is maintained may be adjusted in accordance with storage temperature.

In the process of the present invention for producing a molded product, the molding material may be shaped into a preset form and thereafter the shaped molded product may be subjected to heat curing. Alternatively, the molding material may be shaped into a preset form and simultaneously be subjected to heat curing.

Any of cycloolefins such as cyclobutene, cyclopentene, cyclooctene, cyclododecene, tetrahydroindene and

methylnorbornene (other than norbornene types) ring-opening copolymerizable with the norbornene type cycloolefins may be mixed and used as long as the object of the present invention is not damaged.

Any of resins such as polyimides, saturated polyesters, polyethylenes, rubber type elastomers, acrylic resins, methacrylic resins and vinyl resins may also be mixed and used.

In the present invention, in addition to the essential components metathesis-polymerizable cycloolefin (a monomer which is usually liquid at normal temperature) and metathesis polymerization catalyst (which is usually solid at normal temperature), additives (or third components) such as an antioxidant, a reaction regulator, a filler, a modifier, a release agent, a colorant, a photostabilizer, a flame retardant and a reinforcing material may be added to carry out the reaction, taking account of physical properties, external appearance and operability.

The antioxidant may be added in addition to the portion contained previously in material monomers. The antioxidant may include hindered phenol type antioxidants as exemplified by 2,6-di(*t*-butyl)-4-methylphenol, 2,6-di(*t*-butyl)-4-ethylphenol, stearyl- β -(3,5-di(*t*-butyl)-4-hydroxyphenyl) propionate,

tetrakis-[methylene-3-(3',5'-di(t-butyl)-4'-hydroxyphenyl) propionate] methane,
2,2'-methylenebis(4-methyl-6-t-butylphenol),
2,2'-methylenebis(4-ethyl-6-t-butylphenol),
4,4'-methylenebis(2,6-di(t-butyl)phenol),
1,3,5-trimethyl-2,4,6-tris(3,5-di(t-butyl)-4-hydroxybenzyl)benzene, and
1,3,5-tris(3',5'-di(t-butyl)-4'-hydroxybenzyl)-S-triazine-2,4,6-(1H,3H,5H)trione.

The antioxidant to be added anew may usually be added in an amount not more than 10,000 ppm. It may also be added in an amount more than 10,000 ppm without problems.

Usually, to the general-purpose starting material monomer dicyclopentadiene, an antioxidant such as 2,6-di(t-butyl)-4-methylphenol or 4-t-butylcatechol has already been added in many cases. In the production process of the present invention, this antioxidant may be used as it is, or other antioxidant may be added anew. It may also be removed in some cases.

The reaction regulator may include reaction inhibitors such as triphenylphosphine, tricyclohexylphosphine, tricyclopentylphosphine, tributylphosphine and triisopropylphosphine. It may usually be added in an amount of from 0.001 to 10 parts by weight based on 100 parts by weight of a DCPD resin

solution.

The filler may include, e.g., inorganic fillers such as silica sand, calcium carbonate, aluminum hydroxide and clay, and organic fillers such as wood flour, and polyester or polystyrene beads. It may be used in an amount appropriately determined in accordance with physical properties of polymers and viscosity of semi-cured materials.

The modifier may include, e.g., elastomers, natural rubbers, butadiene rubbers, polymethyl methacrylate, polyvinyl acetate and polystyrene. It may usually be used in an amount ranging from 1 to 50 parts by weight based on 100 parts by weight of the resin, which depends on physical properties of the intended polymers.

The release agent may include, e.g., zinc stearate, silicone oil and fluorine oil. It may usually be added in an amount of from 0.01 to 5 parts by weight based on 100 parts by weight of the resin.

The colorant may include inorganic pigments such as titanium dioxide, cobalt blue and cadmium yellow, and organic pigments such as carbon black, aniline black, phthalocyanine and quinacridone.

As weatherability-providing agents, an ultraviolet light absorber and a photostabilizer are available. The ultraviolet light absorber may include, e.g., salicylic

acid type ultraviolet light absorbers such as phenyl salicylate and para-t-butylphenyl salicylate, benzophenone type ultraviolet light absorbers such as 2,4-dihydroxybenzophenone,

5 2-hydroxy-4-methoxybenzophenone and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, benzotriazole type ultraviolet light absorbers such as 2-(2'-hydroxy-5'-methoxyphenyl)benzotriazole, 2-{2'-hydroxy-3',5'-di(t-butyl)phenyl}benzotriazole and 2-{2'-hydroxy-3',5'-di(t-amyl)phenyl}benzotriazole, and cyanoacrylate type ultraviolet light absorbers such as 2-ethylhexyl-2-cyano-3,3'-diphenyl acrylate and ethyl-2-cyano-3,3'-diphenyl acrylate. Any of these may be used alone or in combination of two or more types.

In order to improve weatherability, a hindered amine type photostabilizer such as bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate and a dimethyl succinate · 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine condensation product may also be added together with the above ultraviolet light absorber.

The flame retardant may include, e.g., halogen type compounds such as hexabromobenzene, tetrabromobisphenol A, decabromodiphenyl oxide, tribromophenol,

dibromophenylglycidyl ether, perchloropentacyclodecane and HET acid derivatives, any of which may be used alone or in combination of two or more types. A phosphoric acid compound such as tris(dichloropropyl) phosphate or tris(dibromopropyl) phosphate or a boric acid compound may also be used in combination. An auxiliary flame retardant, which may include antimony trioxide, iron oxide and aluminum hydride, may further be used in combination with the flame retardant, whereby the flame-retardant effect can be made higher. Usually, the halogen type flame retardant may be used in an amount ranging from 1 to 50 parts by weight, and the auxiliary flame retardant such as antimony trioxide from 1 to 15 parts by weight, based on 100 parts by weight of the resin. Also, hydrates such as aluminum hydroxide and magnesium hydroxide may be used in combination as a filler aiming at flame retardation. Any of these may preferably be added in an amount ranging from 10 to 300 parts by weight based on 100 parts by weight of the resin.

As the reinforcing material, usable are inorganic fiber reinforcing materials such as glass and carbon, PAN, pitch or rayon type carbon fibers, and organic fibers such as PET fibers, polyethylene fibers and Kevlar. These reinforcing materials may be in the form of any of a mat, a roving and a cloth. Any of these reinforcing materials

may be kept mixed in materials, or may previously be set in a mold for molding.

The molding material of the present invention may be used under solvent-free composition, and a solvent may optionally be used.

In the present invention, the molding material is heated to effect polymerization reaction. The heating is usually operated in two stages. The first-stage heating is carried out in order to bring the molding material into a semi-cured state, which may be heated at a temperature of from 0 to 100°C, and preferably from 20 to 40°C, and for a time appropriately determined in accordance with the quantity of the catalyst and the reaction temperature.

The second-stage heating is carried out in order to shape the molding material into a preset form and also to complete the curing. This heating may usually be at a temperature of from 80 to 250°C, and preferably from 100 to 200°C. The reaction time is appropriately determined in accordance with the quantity of the catalyst and the reaction temperature.

The molding material standing semi-cured in the present invention may have any shape of a plate, a sheet or a rod.

As molded products obtained by heat-curing the molding material standing semi-cured may be any of flat

articles or solid articles such as pipes, half-round pipes and laminates.

When a mold for molding is used to shape the molding material into a preset form, a mold for compression molding or a usual mold for SMC (sheet mold compound) or BMC (bulk mold compound) molding may be used. Also, various molding methods such as compression, injection compression and matched metal die molding may be used. Molding methods may appropriately be selected and also the shape and material of a mold may be selected, in accordance with use of molded products and production.

Fig. 1 is an illustration (cross-sectional diagrammatic view) showing how to produce a molded product from a semi-cured material by use of a mold for SMC molding.

Atmosphere in the molding of the present invention may be an atmosphere of air (oxygen and moisture are contained in the atmosphere). Of course, a special measure may be taken such that the atmosphere is displaced with nitrogen gas or the like, but such a measure is not economical.

The present invention will be described below by giving Examples. In the following Examples, "part(s)" refers to "part(s) by weight" unless particularly noted.

Example 1

Commercially available dicyclopentadiene (DCPD) with a purity of 99% by weight was heated to about 35°C. Thereafter, 0.13 part of triphenylphosphine, based on 100 parts of DCPD, was added and dissolved, followed by addition of 0.1 part of the Ru carbene catalyst of formula (3). The resultant mixture was allowed to react while its temperature was maintained at 35°C. At the time the surface of the reaction fluid came into a state where it was stringy when touched with a glass rod of 2 mm diameter (the semi-cured state), this was introduced into a mold for compression molding to carry out molding as described below.

The mold of compression molding was set in a vertically movable hydraulic press, and mold temperature was set at 120°C. As shown in Fig. 1, the semi-cured material was introduced into the mold in the state the mold was opened, and then the hydraulic press was operated to close the mold to carry out molding. Here, the pressure was 80 kg per 1 cm square of flat-plate area. After lapse of about 2 hours, the mold was opened and a molded product was taken out. The molded product obtained was a molded product having sufficient strength and hardness.

Incidentally, used as the mold for compression molding was a mold for SMC flat-plate molding (size of flat plate: 300 mm long, 300 mm wide and 4 mm high). This mold

comprises a bottom force (female mold) and a top force (male mold).

Example 2

A reaction fluid was prepared in the same formulation as in Example 1. This reaction fluid was put in a frame made of aluminum (300 mm long, 300 mm wide and 2 mm deep).

The reaction fluid was put in a 40°C hot chamber together with the frame to carry out reaction. After lapse of 3 hours, a reaction product was taken out of the hot chamber.

Here, the reaction product was in a solid state, having no fluidity. This reaction product was removed from the frame to obtain a molding material standing semi-cured.

This molding material was stored at room temperature for a day, and was thereafter manually wound around the periphery of a glass tube of 50 mm outer diameter so as to be shaped. Next, the molding material thus shaped was put in a curing furnace together with the glass tube, and was allowed to react at 120°C to effect curing. After lapse of 1 hour, the cured product obtained was taken out of the curing furnace, and was removed from the glass tube to obtain a cylindrical (pipe-like) molded product.

POSSIBILITY OF INDUSTRIAL APPLICATION

According to the present invention, molded products

can be produced with ease and in safe by molding carried out in the atmosphere (in the air for which no special treatment is taken), using metathesis-polymerizable cycloolefins as materials. Also, the existing molding machines such as various compression molding apparatus can be utilized.

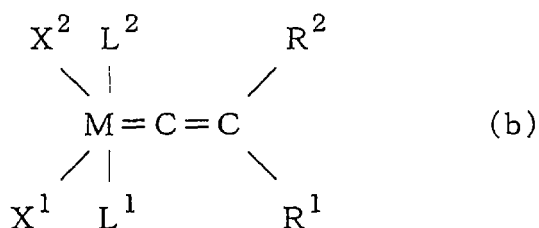
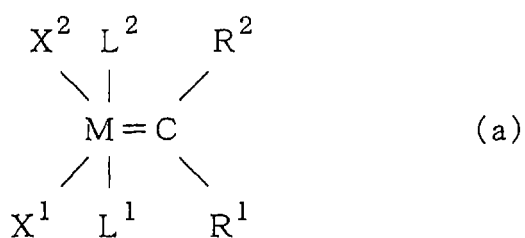
Claims

1. A curable molding material made semi-cured by allowing a metathesis-polymerizable cycloolefin to react in the presence of a metathesis polymerization catalyst.

2. The molding material according to claim 1, which has a shape of at least one selected from a plate, a sheet and a rod.

3. The molding material according to claim 1 or 2, wherein said metathesis-polymerizable cycloolefin is at least one selected from a bicyclic or more-cyclic norbornene and a monocyclic cycloolefin having 4 or more carbon atoms.

4. The molding material according to any one of claims 1 to 3, wherein said metathesis polymerization catalyst is at least one of metathesis polymerization catalysts represented by the following Formulas (a) and (b).



wherein;

M represents a ruthenium atom or an osmium atom;

R¹ and R² each independently represent a group selected from a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, an alkynyl group having 2 to 20 carbon atoms, an aryl group, a carboxylate group having 1 to 20 carbon atoms, an alkoxyl group having 1 to 20 carbon atoms, an alkenyloxy group having 2 to 20 carbon atoms, an aryloxy group, an alkoxycarbonyl group having 2 to 20 carbon atoms, an alkylthio group having 1 to 20 carbon atoms, an alkylsulfonyl group having 1 to 20 carbon atoms, an alkylsulfinyl group having 1 to 20 carbon atoms, an alkylseleno group having 1 to 20 carbon atoms, an alkylseleninyl group having 1 to 20 carbon atoms and an alkylselenonyl group having 1 to 20 carbon atoms, each of which may be substituted with any of an alkyl group having

1 to 5 carbon atoms, a halogen atom, an alkoxyl group having 1 to 5 carbon atoms and phenyls, where the phenyls may be substituted with a halogen atom, an alkyl group having 1 to 5 carbon atoms or an alkoxyl group having 1 to 5 carbon atoms;

X^1 and X^2 each represent an anionic ligand; and

L^1 and L^2 each represent a neutral electron-donating group.

5. A process for producing a molded product, comprising;

a first step of preparing the molding material according to any one of claims 1 to 4; and

a second step of shaping the molding material into a preset form, followed by heat curing.

6. The process for producing a molded product according to claim 5, wherein said second step comprises the steps of;

shaping said molding material into a preset form; and
subjecting the molding material thus shaped, to heat curing;
in this order.

7. The process for producing a molded product

according to claim 5, wherein said second step comprises the step of;

subjecting said molding material to heat curing while shaping said molding material into a preset form.

8. A process for producing a molded product, comprising allowing a metathesis-polymerizable cycloolefin to react in the presence of a metathesis polymerization catalyst to form a molding material standing semi-cured, and introducing the molding material into a molding mold while the molding material is kept semi-cured, followed by curing.

9. The process for producing a molded product according to claim 5 or 8, wherein a mold for compression molding is used as said molding mold.

10. The process for producing a molded product according to any one of claims 5 to 9, wherein the molding is carried out in the atmosphere.